

SCIENCE FOR CERAMIC PRODUCTION

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TECHNOLOGICAL PROPERTIES OF ULTRADISPERSE PLASMOCHEMICAL POWDERS

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The casting properties and the moldability of ultradisperse plasmochemical powders based on aluminum and zirconium oxides are studied after synthesis and annealing at different temperatures. It is demonstrated that after relatively low-temperature annealing it is possible to obtain slip with satisfactory casting properties without a significant increase in the size of crystallites in the powder particles.

Ceramics based on zirconium dioxide currently occupies one of the leading places among ceramic materials used in engineering to manufacture structural products and instruments [1]. This is primarily due to a set of unique properties inherent in ceramics made of zirconium dioxide; due to its transformation under loading, this material has high parameters of strength, destruction viscosity, hardness, and wear resistance.

The methods of plasmochemical synthesis of powders have recently become widely used. These methods make it possible to obtain highly dispersed high-purity powders of a required composition with homogeneous distribution of components and mean particle size below 20 nm [2].

Plasmochemical powders, as a rule, have a large specific area (over 15 m²/g), which determines their morphological structure and makes it unfavorable for the molding process. At the same time, their sintering activity is so high that it is not always possible to obtain homogenous shrinkage in the whole volume and, consequently, a homogenous density after sintering, which, as a rule, causes fragmentation (cracking) of articles in the course of sintering.

On the other side, it is inadvisable to use the known molding method based on thermoplastic slip [3] in this case, since slip preparation requires a high amount of binding agent, due to the large specific surface area of such systems.

It is possible to change the situation by subjecting plasmochemical powders to preliminary low-temperature annealing, which will decrease the specific surface area without modifying the particle size. In this case, one can expect a

substantial decrease in the quantity of the binder introduced into the powder for the preparation of thermoplastic slip.

The purpose of the present study was to investigate the casting properties and the moldability of plasmochemical powders after synthesis and annealing at different temperatures intended for the production of thermoplastic slip.

The object of the study was powders produced by decomposition of aqueous solutions of Al, Zr, and Y salts in high-frequency discharge plasma. The powder composition was (wt.%): 100 Al₂O₃, ZrO₂ (3Y₂O₃) + 20 Al₂O₃. The morphological study of the powders was carried out employing a BS-500 Tesla electron microscope using the carbon replica method. The powders were annealed in air at temperatures 1000 – 1600°C for 30 min.

A thermoplastic slip was prepared from the initial and annealed powders on a Gart unit. For the purpose of reference of the technological properties of the slip, the standard slip grades VK-94 and 22KhS, widely applied in production were used.

The main technological parameter of a slip is its casting capacity, which is the integrated index of viscosity and solidification rate. This value is characterized by the height of filling a channel of a specified section. The casting capacity of different slips, as a rule, is determined for the constant conditions: slip temperature 65°C, pressure 0.2 MPa (2 at), and mold temperature 20°C [4].

To obtain thermoplastic slips, the initial and annealed powders were mixed with a surfactant for 16 h. After mixing, the powders were sifted, and a technological binder (paraffin) was introduced. The amount of paraffin was chosen in a way to ensure equal viscosity in all systems within the limits

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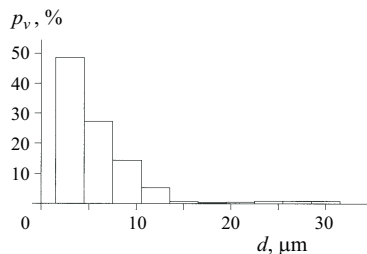


Fig. 1. Distribution p_v of powder particles by size d .

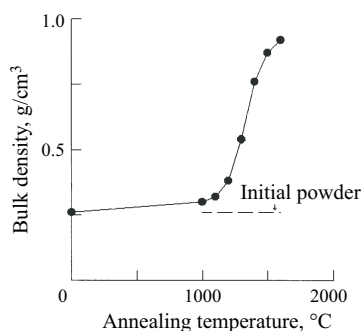


Fig. 2. Variations in bulk density of ZrO_2 powder depending on the annealing temperature.

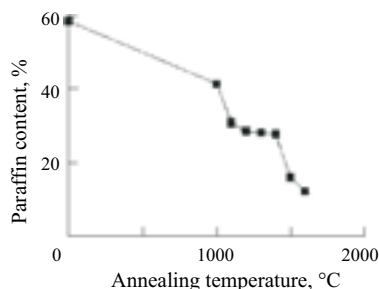


Fig. 3. Quantity of paraffin introduced into powder versus the annealing temperature.

of $0.4 - 0.5 \text{ Pa} \cdot \text{sec}$, which ensures good casting properties [5].

The analysis of the powders after plasmochemical synthesis indicated that they consist of hollow and filled spheres, fragments of these spheres, and transparent agglomerates of the foam type. The distribution of powder particles of the composition $\text{ZrO}_2 (3\% \text{ Y}_2\text{O}_3) + 20\% \text{ Al}_2\text{O}_3$ based on sedimentation analysis data is represented in Fig. 1. It can be seen that the majority of the agglomerated powder particles have a particle size not exceeding $10 \mu\text{m}$, whereas the mean size is $3.1 \mu\text{m}$.

The powder in its initial state has a low bulk density (the horizontal dashed line in Fig. 2). Annealing at a temperature below 1000°C does not lead to substantial variations in the bulk density. A temperature increase up to $1200 - 1300^\circ\text{C}$

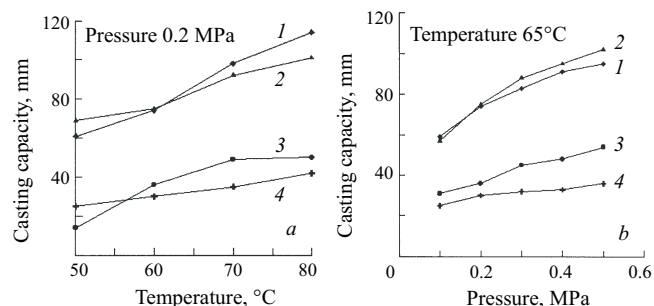


Fig. 4. Casting capacity of slip versus temperature (a) and working pressure (b): 1 and 4) slips VK-94 and 22KhS, respectively; 2 and 3) based on powders Al_2O_3 and ZrO_2 .

causes an insignificant elevation of the bulk density, and annealing at a temperature above 1300°C abruptly increases it.

The electron microscopic study of the annealed powders indicated that starting with the temperature 1200°C , intense recrystallization takes place in the powder, the hollow spheres and transparent polycrystalline films are no longer registered, and the powder particles agglomerate in chains and acquire faces. With an increase in the annealing temperature, the type of electron patterns changes as well. As distinct from the initial powder, the electron pattern of powder annealed at temperature 1200°C is a point pattern. It was impossible to obtain the electron patterns of the powders annealed at $1300 - 1500^\circ\text{C}$, since the considered powder particles became opaque, as a consequence of their growth.

Figure 3 shows the dependence of the quantity of the binder introduced in the powder on the annealing temperature. As the firing temperature increases, the amount of the binder required for the preparation of a slip becomes perceptibly smaller, and with annealing temperatures over 1500°C , less than 20% binder is required. However, such a slip does not have the required technological properties, since the powder particles become large, and the slip loses stability: when stored in the melted state, the slip becomes stratified, i.e. the large particles sink, and pure paraffin emerges on the surface. Even after thorough mixing at the casting temperature, the stratification of a slip occurs already in 1 – 2 min. The products obtained from such a slip have a low packing coefficient, which later leads to increased final porosity; therefore, slips with such low stability and packing coefficient are not suitable for industrial production.

Figure 4 shows the dependences of the casting capacity of the slips prepared from plasmochemical powders, as well as the standard slips VK-94 and 22KhS, on the temperature and working pressure. As can be seen, with increasing temperature and working pressure, the casting capacity of all slips grows, although such increase in slip 22KhS and the slip based on $\text{ZrO}_2 (3\% \text{ Y}_2\text{O}_3) + 20\% \text{ Al}_2\text{O}_3$ is insignificant. The maximum casting capacity is registered in slip VK-94 and the slip made of the plasmochemical Al_2O_3 powder, on varying both the temperature and the working pressure. The casting capacity of 22KhS slip and the slip based on the pow-

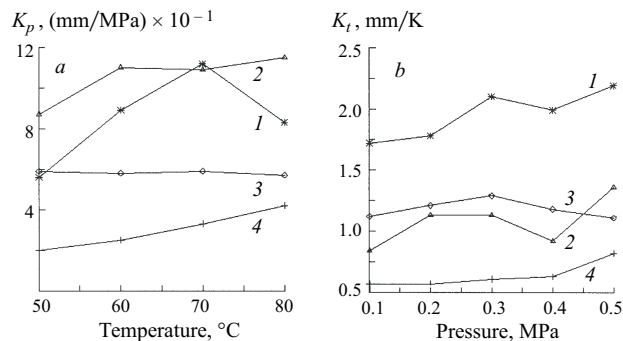


Fig. 5. Dependence of the casting capacity coefficient of slip on temperature K_p (a) and working pressure K_t (b). Same designations as in Fig. 4.

ders ZrO_2 (3% Y_2O_3) + 20% Al_2O_3 is somewhat lower, although sufficient for production of various articles.

The rate of change in the casting capacity of a slip (casting capacity coefficient) depending on temperature and working pressure is shown in Fig. 5. The casting capacity coefficient of slip 22KhS has the minimum values and grows to some extent with increasing temperature, whereas in varying the pressure level, this coefficient grows (insignificantly) only at the maximum pressure values and is only weakly related to both temperature and working pressure. The casting capacity factor of the slip based on the powders ZrO_2 (3% Y_2O_3) + 20% Al_2O_3 is higher than that of slip 22KhS and the slip based on Al_2O_3 and is virtually independent of the temperature, although it becomes slightly lower with increasing pressure. The maximum values of the casting capacity factor registered in slip VK-94 ensure its good technological parameters.

Another important technological property of powders is moldability. It is known that the dependence of density on molding pressure can be described by the power function [3]:

$$P = P_0 \theta^m,$$

where P is the current pressure; P_0 is the pressure needed to accomplish the pore-free state; θ is the relative density; m is the moldability index.

In order to determine the moldability of initial and annealed powders, they were placed in a steel mold and loaded to the pressure 1 GPa while recording the powder compaction curve. The obtained data were used to construct the dependence of density on molding pressure in double logarithmic coordinates (Fig. 6). Annealing at a temperature below

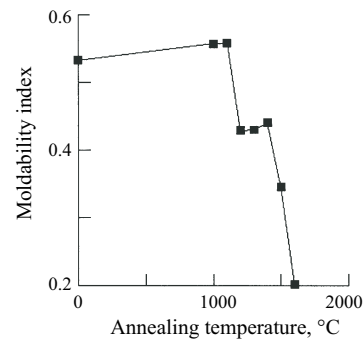


Fig. 6. Powder moldability index depending on the annealing temperature.

1200°C virtually does not change the bulk density and prevents reaching a density level more than 50% of the theoretical density, even under a pressure of 1 GPa. An increase in the powder annealing temperature leads to a substantial increase in the final density of samples, especially at low pressures.

As the result of studying the dependence of the moldability index on the annealing temperature, it was found that only initial powders and powders annealed at a temperature below 1200°C have satisfactory moldability. With the annealing temperature above 1300°C, the moldability index abruptly decreases, since the powder sinters in the form of large conglomerates which are hard to destroy in molding.

Thus, ultradisperse plasmochemical powders based on zirconium and aluminum oxides after relatively low-temperature annealing can be used to produce slips with satisfactory casting properties without substantial increase in the size of crystallites in powder particles.

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